Preparation of Alkanesulfenamides by Selective Elimination of *t*-Butyl Group in *S*-Alkyl-*S*-*t*-butylsulfilimines

Tamotsu YAMAMOTO,* Masa-aki KAKIMOTO,† Takeshi MAEJIMA, and Makoto OKAWARA†

Department of Industrial Chemistry, Faculty of Engineering, Kanto Gakuin University, Mutsuura, Kanazawa-ku, Yokohama 236

†*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 227*

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Synopsis. *N*-Tosylalkanesulfenamides have been prepared *via* the reactions of alkyl halides with 2-methyl-2-propanethiolate followed by *S*-imination with chloramine T and the thermolysis. This method comprises the use of selective elimination of *t*-butyl group in *S*-alkyl-*S*-*t*-butylsulfilimines.

Sulfenamides are useful compounds as synthetic intermediates, sulfenating agents, and as industrial additives such as accelerators in rubber vulcanization, pesticides, fungicides, and radioprotective agents.

Up to the present various kinds of sulfenamides have been prepared. Among them, only a few examples of alkanesulfenamides[1] have been synthesized because of their instability and unavailability of the corresponding sulfenyl source.

On the other hand, the thermolysis of the sulfilimines which have one or more hydrogens at β-carbon has been known to give an effective, preparative route to olefins[2] and vinyl monomers.[3] Since the thermolysis gives arenesulfenamides in good yields at the same time, it seems to be an effective route to alkanesulfenamides. No active attempt to prepare labile alkanesulfenamides, however, has been made. Thus, to prepare alkanesulfenamides by the thermolysis under mild conditions, the use of *t*-butyl group being liable to eliminate as isobutylene has been undertaken.

For this purpose *S*-alkyl-*S*-*t*-butyl-*N*-tosylsulfilimines were prepared and thermolyzed as follows. First alkyl *t*-butyl sulfides were prepared by the reaction of alkyl halides (**1**) with 2-methyl-2-propanethiol in a phase transfer system. Subsequently sulfides (**2**) were allowed to react with chloramine T (CT) to give *S*-alkyl-*S*-*t*-butyl-*N*-tosylsulfilimines (**3**) in high yields. The structures of sulfilimines **3** were confirmed by IR and NMR spectra and elemental analyses. The results obtained are given in Table 1.

$$\underset{\mathbf{1}}{RX} + t\text{-BuSH} \xrightarrow{NaOH/H_2O\text{-}PTC} \underset{\mathbf{2}}{RS\text{-}t\text{-}Bu} \xrightarrow{CT} \underset{\mathbf{3}}{\begin{matrix} R \\ \diagdown \\ t\text{-Bu}\diagup \end{matrix}\!\!S{=}NTs}$$

The thermolysis of **3** was carried out in methanol (at 40 °C or 60 °C), benzene (under refluxing) or without solvent (at 10 °C above mp of **3**). The thermolysis in refluxing benzene gave the best result, affording *N*-tosylalkanesulfenamide (**4**) accompanied with *N*-tosyl-2-methyl-2-propanesulfenamide (**5**) in some cases.

$$\underset{\mathbf{3}}{\begin{matrix} R \\ \diagdown \\ t\text{-Bu}\diagup \end{matrix}\!\!S{=}NTs} \xrightarrow{\Delta} \underset{\mathbf{4}}{RS\text{-}NHTs} \text{ or (and) } \underset{\mathbf{5}}{t\text{-BuS-NHTs}}$$

Thus *S*-*t*-butyl-*S*-ethyl-*N*-tosylsulfilimine (**3a**) was thermolyzed in refluxing benzene for 4 h to give *N*-tosylethanesulfenamide (**4a**) quantitatively. Similarly the other sulfilimines, *S*-*t*-butyl-*S*-propyl-, *S*-butyl-*S*-*t*-butyl-, and *S*-*t*-butyl-*S*-hexyl-*N*-tosylsulfilimines (**3b**, **3c**, and **3d**), were thermolyzed to give the corresponding *N*-tosylalkanesulfenamides, *N*-tosyl-1-propane-, -2-butane-, and -1-hexanesulfenamides (**4b**, **4c**, and **4d**) in quantitative yields, respectively. These sulfenamides were almost pure as shown by their sharp mp's and spectral data without purification. These are so stable as to be stored in sealed bottles at room temperature or preferably at lower temperature in an ice box. With *S*-*t*-butyl-*S*-isopropyl-*N*-tosylsulfilimine (**3e**), two kinds of sulfenamides, *N*-tosyl-2-propane- and 2-methyl-2-propanesulfenamides (**4e** and **5**), were obtained as a mixture with the molar ratio (**4e** to **5**) of about 5, which was determined by NMR and mass spectroscopies. These results are given in Tables 2 and 3. As shown in Table 2, the selectivity of eliminating either *t*-butyl or alkyl group is remarkably exclusive for the former.

TABLE 1. THE RESULTS OF THE PREPARATION OF **3**

R	Mp θ_m/°C	Yield/%	IR $\tilde{\nu}$/cm^{-1} $\nu_{S=N}$	IR ν_{SO_2}	NMR δ in $CDCl_3$	Found(Calcd)(%) C	H	N
a C_2H_5	108—109	78	960	1280 1130	1.10 (t, 3H) 1.28 (s, 9H) 2.40 (s, 3H) 2.72 (q, 2H) 7.24 (d, 2H) 7.80 (d, 2H)	54.03 (54.31)	7.31 (7.38)	4.81 (4.87)
b C_3H_7	83—84	79	970	1279 1134	0.89 (t, 3H) 1.28 (s, 9H) 1.1—1.8(m, 2H) 2.40 (s, 3H) 2.4—2.8(t, 2H) 7.20 (d, 2H) 7.72 (d, 2H)	55.53 (55.77)	7.90 (7.70)	4.82 (4.65)
c C_4H_9	102—103	77	969	1280 1132	0.76 (t, 3H) 1.28 (s, 9H) 1.1—2.0(m, 4H), 2.40 (s, 3H) 2.64 (m, 2H) 7.20 (d, 2H) 7.76 (d, 2H)	56.85 (57.09)	8.30 (8.00)	4.65 (4.44)
d C_6H_{13}	103—104	98	960	1280 1135	0.88 (t, 3H) 1.32 (s, 9H) 1.0—2.1 (m, 8H) 2.44 (s, 3H) 2.68 (m, 2H) 7.24 (d, 2H) 7.80 (d, 2H)	59.27 (59.42)	8.48 (8.52)	4.20 (4.08)
e *i*-C_3H_7	96—97	87	990	1283 1127	1.20 (d, 6H) 1.28 (s, 9H) 2.44 (s, 3H) 3.22 (m, 1H) 7.20 (d, 2H) 7.78 (d,2H)	55.68 (55.77)	8.00 (7.70)	4.55 (4.65)

Table 2. The results of thermolyses of 3's in refluxing benzene for 4 h

3 R–S=NTs (t-Bu, R)		Mp θ_m/°C	4 Yield %	Mass (M^+) (m/e)	Composition(%) 4	5
a	C_2H_5	64—65	≃100	231	≃100	≃0
b	C_3H_7	59—60	≃100	245	≃100	≃0
c	C_4H_9	38—38.5	≃100	259	≃100	≃0
d	C_6H_{13}	34—35	≃100	287	≃100	≃0
e	i-C_3H_7	79—80	83	245	83	17

Table 3. NMR spectra of 4

	NMR ($CDCl_3$) δ
4a	1.26 (t, 3H) 2.46 (s, 3H) 2.80 (q, 2H) 6.26 (s, 1H) 7.30 (d, 2H) 7.80 (d, 2H)
4b	0.97 (t, 3H)1.4—2.2 (m, 2H) 2.45 (s, 3H) 2.72 (t, 2H) 6.27 (s, 1H) 7.37 (d, 2H) 7.90 (d, 2H)
4c	0.88 (t, 3H) 1.1—1.9 (m, 4H) 2.44 (s, 3H) 2.74 (t, 2H) 6.26 (s, 1H) 7.29 (d, 2H) 7.80 (d, 2H)
4d	0.88 (t, 3H) 1.0—1.8 (m, 8H) 2.44 (s, 3H) 2.72 (t, 2H) 6.20 (s, 1H) 7.26 (d, 2H) 7.78 (d, 2H)
4e	1.24 (d, 6H) 2.46 (s, 3H) 3.28 (m, 1H) 6.33 (s, 1H) 7.28 (d, 2H) 7.78 (d, 2H)

The procedure mentioned above may be an effective method, starting from alkyl halides, to prepare alkanesulfenamides *via* alkyl *t*-butyl sulfides and then sulfilimines, in good yields, and further a convenient route to other *N*-substituted alkanesulfenamides by the exchange reaction with amines.[4]

Experimental

Preparation of 3. *General Procedure*: To a stirring solution of chloramine T (11 mmol) in 30 ml of MeOH was added 10 mmol of **2**, which was prepared from the corresponding halide **1**, 2-methyl-2-propanethiol and NaOH in water containing tetrabutylammonium bromide (1%), keeping the temperature below 20 °C (0 °C for **3e**). After 3—4 h stirring the resulting mixture was evaporated to dryness *in vacuo*. The organic part in the residue obtained was dissolved in 30 ml of $CHCl_3$, and the solution was washed with water and dried over anhydrous Na_2SO_4. After the dried solution was evaporated to dryness *in vacuo*, the resulting viscous residue was triturated with ether until the white solid of **3** was deposited. Crude **3** was collected by filtration and purified by reprecipitation from CH_2Cl_2 and ether.

Thermolysis of 3. *General Procedure*: To 20 ml of dried benzene was added 2 mmol of **3**. The resulting mixture was heated under refluxing in a stream of nitrogen. After 4 h the solution obtained was evaporated to dryness under reduced pressure to give white solid of **4**. Sulfenamide **4** obtained in such a manner was almost pure without purification. For the purification of crude **4**, reprecipitation using dried ether and hexane was taken.

References

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